An Efficient and Convenient Method for the Direct Conversion of Alkyl Silyl Ethers into the Corresponding Alkyl Ethers Catalyzed by Iron(III) Chloride

Katsuyuki Iwanami, Kentaro Yano, Takeshi Oriyama*

Faculty of Science, Ibaraki University, 2-1-1 Bunkyo, Mito 310-8512, Japan
Fax +81(29)2288403; E-mail: tor@mx.ibaraki.ac.jp

Received 23 March 2005; revised 12 May 2005

Abstract: Various alcohol silyl ethers were readily and efficiently transformed into the corresponding alkyl ethers in high yields by the use of aldehydes combined with triethylsilane in the presence of a catalytic amount of iron(III) chloride.

Key words: silyl ether, alkyl ether, protecting group, iron(III) chloride, reductive etherification

Alkyl ethers such as benzyl ethers and substituted benzyl ethers are indispensable functional groups in synthetic organic chemistry, and have been used among a wide range of protecting groups of the hydroxyl function.[1] Dialkyl ethers are generally formed by the treatment of the parent alcohols with the corresponding alkyl halides under the influence of a base such as sodium hydride,[2] sodium hydroxide,[3] and so on. Direct transformations between various typical protecting groups of the hydroxyl function are of great importance from the point of view of green chemistry, economy of time and reagents. In the series of our studies on the direct conversion between various types of protecting groups of the hydroxyl function (Figure 1),[4] we have previously demonstrated that direct conversion of aryl trialkylsilyl ethers into the corresponding aryl benzyl ethers can be conveniently performed by reaction with benzyl bromide in the presence of cesium fluoride.[4f] Although direct transformation of silyl ethers into the corresponding alkyl ethers is known to be possible using the method of reductive etherification,[5] the starting silyl ethers of almost all examples are limited to trimethylsilyl ethers.

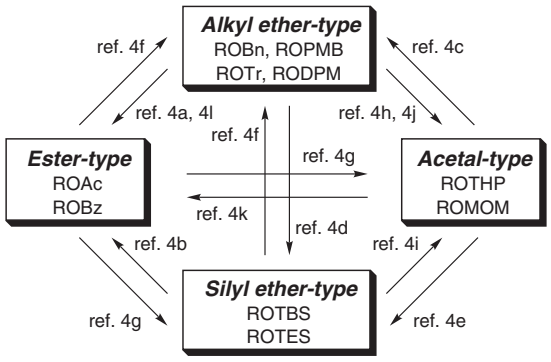


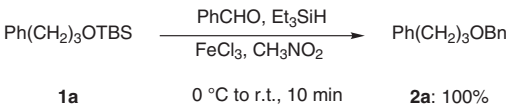
Figure 1 Direct conversion between typical protecting groups of the hydroxyl function (DPM = Ph_2CH).

SYNTHESIS 2005, No. 16, pp 2669–2672
Advanced online publication: 04.08.2005
DOI: 10.1055/s-2005-872120; Art ID: F05505SS

Herein, we wish to report an efficient and convenient method for the direct conversion of alkyl silyl ethers into the corresponding alkyl ethers catalyzed by iron(III) chloride in a one-pot procedure. In the course of our exploration of the usefulness of the reactions promoted by iron(III) chloride,[6] quite recently, we have developed a highly efficient reductive etherification of aldehydes with alkoxytrimethylsilane and triethylsilane catalyzed by iron(III) chloride.[6d] Next, we applied this reductive etherification into the direct conversion of silyl-protected alcohols into alkyl-protected alcohols.

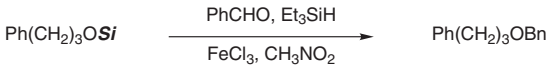
First, we undertook to examine the conversion of the *tert*-butyldimethylsilyl ether of 3-phenylpropanol into the corresponding benzyl ether. A mixture of silyl ether **1a**, benzaldehyde, and 5 mol% of iron(III) chloride was treated with triethylsilane in nitromethane for ten minutes. The usual work-up of the reaction mixture afforded the desired benzyl ether **2a** in quantitative yield as shown in Scheme 1.

Next, we tested the effect of the trialkylsilyl moiety of silyl ethers (Table 1). In the case of triethylsilyl (TES) and *tert*-butyldimethylsilyl (TBS) ether, the corresponding benzyl ethers could be obtained in quantitative yield (en-



Scheme 1 Benzyl etherification of TBS ether of 3-phenylpropanol (molar ratio of silyl ether:aldehyde:Et_3SiH:$FeCl_3$ = 1:1.2:1.2:0.05)

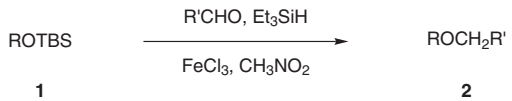
Table 1 Synthesis of Benzyl Ethers from Various Silyl Ethers of 3-Phenylpropanol[a]



Entry	$Ph(CH_2)_3OSi$	Temp (°C)	Time	Yield of **2a** (%)[b]
1	$Ph(CH_2)_3OTES$	0	2 h	quant
2	$Ph(CH_2)_3OTBS$	0 to r.t.	10 min	quant
3	$Ph(CH_2)_3OTIPS$	0	24 h	71
4	$Ph(CH_2)_3OTBDPS$	0	24 h	37

[a] Molar ratio of silyl ether:aldehyde:Et_3SiH:$FeCl_3$ = 1:1.2:1.2:0.05.
[b] Isolated yield of purified product.

Table 2 Synthesis of Various Benzyl and Substituted Benzyl Ethers from Alcohol TBS Ethers[a]



1 **2**

Entry	ROTBS	R′CHO	Temp (°C)	Time (min)	Product	Yield (%)[b]
1	$Ph(CH_2)_2CH_2OTBS$	PhCHO	0 to r.t.	10	**2a**	quant
2[c]		4-$MeOC_6H_4CHO$	–20	80	**2b**	88
3[c]		2-$MeOC_6H_4CHO$	0	30	**2c**	96
4		4-$NO_2C_6H_4CHO$	0	45	**2d**	97
5		4-BrC_6H_4CHO	0	30	**2e**	quant
6		4-NCC_6H_4CHO	0 to r.t.	30	**2f**	92
7	$Ph(CH_2)_2CH(Me)OTBS$	PhCHO	0 to r.t.	15	**2g**	quant
8[c]		4-$MeOC_6H_4CHO$	–20	240	**2h**	76
9[c]		2-$MeOC_6H_4CHO$	0	60	**2i**	89
10		4-$NO_2C_6H_4CHO$	0 to r.t.	120	**2j**	92
11		4-BrC_6H_4CHO	0	180	**2k**	92
12	*cyclo*-$C_6H_{11}OTBS$	PhCHO	0 to r.t.	40	**2l**	80
13	$Ph(CH_2)_2C(Me)_2OTBS$	PhCHO	0	60	**2m**	30
14	PhOTBS	PhCHO	r.t.	90	–	0
15	$BnO(CH_2)_6OTBS$	PhCHO	0	30	**2n**	83
16	$BzO(CH_2)_6OTBS$	PhCHO	0	180	**2o**	88
17[d]	$TBSOCH_2CH(OBz)(CH_2)_2OTBS$	PhCHO	0 to r.t.	10	**2p**	80

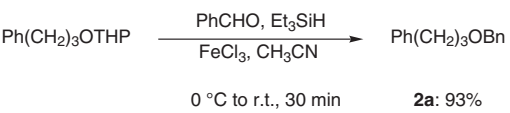
[a] Molar ratio of silyl ether:aldehyde:Et_3SiH:$FeCl_3$ = 1:1.2:1.2:0.05, unless otherwise noted.
[b] Isolated yield of purified product.
[c] CH_3CN was used as a solvent.
[d] 2.4 Equiv of aldehyde and 2.4 equiv of Et_3SiH was used.

tries 1 and 2). On the other hand, the reactions of more sterically hindered trialkyl silyl ethers, triisopropylsilyl (TIPS) and *tert*-butyldiphenylsilyl (TBDPS) ether, did not proceed smoothly under comparable reaction conditions (entries 3 and 4).

The direct conversion was conducted with various TBS ethers of primary, secondary, tertiary, and phenolic alcohols and the successful results are summarized in Table 2.

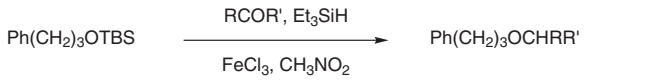
The TBS ether of a secondary alcohol was converted to the corresponding benzyl ether quantitatively (entry 7). It should be noted that various *para*-substituted benzyl ethers, which are purposeful protecting groups for a hydroxyl function, are obtained in high to excellent yields by the use of the corresponding *para*-substituted benzaldehyde instead of benzaldehyde (entries 2–6, 8–11). On the other hand, the TBS ether of a tertiary alcohol gave the desired product in only 30% yield (entry 13). In the case of silyl ether of phenol, the expected reaction did not proceed at all (entry 14). Furthermore, in the presence of other types of protective groups such as benzyl ether and benzoate, TBS ethers are chemoselectively transformed into the corresponding benzyl ethers in satisfactory yields (entries 15–17). And besides, migration of benzoyl group was not observed (entry 17). In contrast, tetrahydropyranyl (THP) ether was also converted into the corresponding benzyl ether **2a** (Scheme 2).

Furthermore, we examined the direct conversion of TBS ethers into various alkyl ethers using various carbonyl compounds instead of benzaldehyde as shown in Table 3. Use of propionaldehyde and valeraldehyde afforded the corresponding *n*-propyl and *n*-pentyl ethers in 73 and 86% yield, respectively (entries 1 and 2). On the other hand, when ketone was used as the carbonyl compound, the cor-



Scheme 2 Benzyl etherification of tetrahydropyranyl ether of 3-phenylpropanol (molar ratio of silyl ether:aldehyde:Et_3SiH:$FeCl_3$ = 1:1.2:2.2:0.05).

Table 3 Synthesis of Various Ethers from TBS Ether of 3-Phenylpropanol[a]



Entry	RCOR′	Time (min)	Product	Yield (%)[b]
1	EtCHO	30	**2q**	73
2	*n*-BuCHO	30	**2r**	86
3	benzylacetone	60	**2s**	91
4	cyclohexanone	60	**2t**	88

[a] Molar ratio of silyl ether:aldehyde:Et_3SiH:$FeCl_3$ = 1:1.2:1.2:0.05. The reaction was performed at 0 °C.
[b] Isolated yield of purified product.

responding secondary alkyl ether was obtained in high yield (entries 3 and 4).

In conclusion, the present reaction has the following synthetic advantages: 1) in contrast to the known procedure of reductive etherification, this one-pot procedure can use not only TMS ether but also TES and TBS ethers as the starting silyl ether; 2) various ethers are obtained from a wide range of aldehydes and ketones; 3) high-yielding process; 4) extremely mild reaction conditions; and 5) experimental convenience. In our series of studies on the direct conversion between typical protecting groups of the hydroxyl function, we have added a new direct transformation of the silyl ether type protecting group of alcohol into an alkyl ether type.

All reactions were carried out under argon. ^1H and ^{13}C NMR spectra were recorded on a JEOL GSX-400 spectrometer at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm (δ) relative to tetramethylsilane in $CDCl_3$. IR spectra were recorded in cm^{-1} on a JASCO FT/IR-300E spectrometer. $FeCl_3$ was purchased from Aldrich and used without further purification. Nitromethane was dried over MS 4Å prior to use. TLC was performed on Wakogel B-5F silica gel with Et_2O and hexane as eluents.

1-Benzyloxy-3-phenylpropane (2a); Typical procedure
To a suspension of anhyd $FeCl_3$ (5.0 mg, 0.031 mmol) and benzaldehyde (76 μL, 0.75 mmol) in nitromethane was added *tert*-butyldimethylsilyl ether of 3-phenylpropanol (155.4 mg, 0.62 mmol) and triethylsilane (120 μL, 0.751 mmol) successively at 0 °C under argon. After stirring for 10 min at r.t., the mixture was quenched with a phosphate buffer (pH 7). The organic materials were extracted with CH_2Cl_2, washed with brine, and dried (Na_2SO_4). 1-Benzyloxy-3-phenylpropane (**2a**; 139.8 mg, quant) was isolated by TLC on silica gel.

Products **2a**,[4h,7,8] **2b**,[4h,8] **2d**, [2,4h] and **2l**[9] had data identical to that reported in the literature.

1-(2-Methoxybenzyloxy)-3-phenylpropane (2c)
IR (neat): 2936, 1492, 1458, 1243, 1097, 1031, 752, 699 cm^{-1}.

^1H NMR: δ = 1.95 (tt, *J* = 7.7, 6.2 Hz, 2 H), 2.72 (t, *J* = 7.7 Hz, 2 H), 3.53 (t, *J* = 6.2 Hz, 2 H), 3.83 (s, 3 H), 4.55 (s, 2 H), 6.95–6.98 (m, 2 H), 7.15–7.40 (m, 7 H).

^{13}C NMR: δ = 31.41, 32.40, 55.30, 67.55, 69.62, 110.07, 120.32, 125.59, 126.86, 128.17, 128.40, 128.72, 141.99, 156.91.

1-(4-Bromobenzyloxy)-3-phenylpropane (2e)
IR (neat): 2857, 1488, 1102, 1070, 1011, 699 cm^{-1}.

^1H NMR: δ = 1.93 (tt, *J* = 7.7, 6.2 Hz, 2 H), 2.71 (t, *J* = 7.7 Hz, 2 H), 3.47 (t, *J* = 6.2 Hz, 2 H), 4.44 (s, 2 H), 7.15–7.29 (m, 7 H), 7.45–7.49 (m, 2 H).

^{13}C NMR: δ = 31.32, 32.37, 69.58, 72.10, 121.26, 125.71, 128.24, 128.35, 129.15, 131.36, 137.50, 141.73.

1-(4-Cyanobenzyloxy)-3-phenylpropane (2f)
IR (neat): 2941, 2861, 2228, 1496, 1454, 1364, 1103, 820 cm^{-1}.

^1H NMR: δ = 1.96 (tt, *J* = 7.7, 6.2 Hz, 2 H), 2.73 (t, *J* = 7.7 Hz, 2 H), 3.51 (t, *J* = 6.2 Hz, 2 H), 4.54 (s, 2 H), 7.16–7.30 (m, 5 H), 7.44 (d, *J* = 8.1 Hz, 2 H), 7.63 (d, *J* = 8.1 Hz, 2 H).

^{13}C NMR: δ = 31.18, 32.38, 67.00, 71.80, 111.01, 118.77, 125.74, 127.53, 128.23, 128.29, 132.05, 141.51, 144.06.

3-Benzyloxy-1-phenylbutane (2g)
IR (neat): 2927, 2861, 1496, 1453, 1134 1092, 1065, 697 cm^{-1}.

^1H NMR: δ = 1.22 (d, *J* = 5.9 Hz, 3 H), 1.70–1.80 (m, 1 H), 1.87–1.97 (m, 1 H), 2.61–2.70 (m, 1 H), 2.72–2.80 (m, 1 H), 3.53 (s, 1 H), 4.43 (d, *J* = 11.7 Hz, 1 H), 4.57 (d, *J* = 11.7 Hz, 1 H), 7.14–7.37 (m, 10 H).

^{13}C NMR: δ = 19.66, 31.85, 38.48, 70.32, 74.08, 125.58, 127.34, 127.59, 128.21, 128.25, 128.32, 138.88, 142.25.

3-(4-Methoxybenzyloxy)-1-phenylbutane (2h)
IR (neat): 2931, 1612, 1512, 1456, 1248, 1035, 699 cm^{-1}.

^1H NMR: δ = 1.21 (d, *J* = 6.2 Hz, 3 H), 1.69–1.79 (m, 1 H), 1.85–1.95 (m, 1 H), 2.58–2.79 (m, 2 H), 3.47–3.56 (m, 1 H), 3.80 (s, 3 H), 4.38 (d, *J* = 11.4 Hz, 1 H), 4.51 (d, *J* = 11.4 Hz, 1 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 7.14–7.29 (m, 7 H).

^{13}C NMR: δ = 19.68, 31.87, 38.48, 55.26, 69.96, 73.72, 113.67, 125.57, 128.20, 128.33, 129.15, 130.99, 142.30, 158.93.

3-(2-Methoxybenzyloxy)-1-phenylbutane (2i)
IR (neat): 2929, 1602, 1494, 1464, 1243, 1074, 753 cm^{-1}.

^1H NMR: δ = 1.23 (d, *J* = 6.2 Hz, 3 H), 1.70–1.80 (m, 1 H), 1.88–1.97 (m, 1 H), 2.62–2.81 (m, 2 H), 3.51–3.60 (m, 1 H), 3.83 (s, 3 H), 4.49 (d, *J* = 12.5 Hz, 1 H), 4.62 (d, *J* = 12.5 Hz, 1 H), 6.86 (d, *J* = 8.1 Hz, 1 H), 6.95 (t, *J* = 7.3 Hz, 1 H), 7.14–7.28 (m, 6 H), 7.42 (d, *J* = 8.1 Hz, 1 H).

^{13}C NMR: δ = 12.77, 31.84, 38.58, 55.24, 65.15, 74.24, 110.01, 120.34, 125.51, 127.36, 128.18, 128.30, 128.37, 128.81, 142.48, 156.86.

3-(4-Nitrobenzyloxy)-1-phenylbutane (2j)
IR (neat): 2928, 2861, 1604, 1520, 1345, 1092, 739 cm^{-1}.

^1H NMR: δ = 1.26 (d, *J* = 5.9 Hz, 3 H), 1.76–1.86 (m, 1 H), 1.91–2.01 (m, 1 H), 2.65–2.81 (m, 2 H), 3.52–3.60 (m, 1 H), 4.52 (d, *J* = 13.2 Hz, 1 H), 4.67 (d, *J* = 13.2 Hz, 1 H), 7.15–7.30 (m, 5 H), 7.50 (d, *J* = 8.8 Hz, 2 H), 8.19 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR: δ = 19.58, 31.82, 38.29, 69.10, 75.05, 123.49, 125.75, 127.55, 128.27, 128.31, 141.90, 146.65.

3-(4-Bromobenzyloxy)-1-phenylbutane (2k)
IR (neat): 2927, 2862, 1488, 1134, 1070, 1011, 804 cm^{-1}.

^1H NMR: δ = 1.22 (d, *J* = 5.9 Hz, 3 H), 1.71–1.80 (m, 1 H), 1.86–1.96 (m, 1 H), 2.61–2.79 (m, 2 H), 3.47–3.56 (m, 1 H), 4.38 (d,

J = 12.1 Hz, 1 H), 4.52 (d, *J* = 12.1 Hz, 1 H), 7.14–7.29 (m, 7 H), 7.46 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR: δ = 19.61, 31.80, 38.36, 69.51, 74.28, 121.14, 125.64, 128.24, 128.28, 129.17, 131.31, 137.89, 142.06.

3-Benzyloxy-3-methyl-1-phenylbutane (2m)
IR (neat): 2971, 1496, 1454, 1090, 1062, 734, 697 cm^{-1}.

^{1}H NMR: δ = 1.32 (s, 6 H), 1.86–1.91 (m, 2 H), 2.70–2.75 (m, 2 H), 4.47 (s, 2 H), 7.15–7.39 (m, 10 H).

^{13}C NMR: δ = 25.83, 30.43, 42.44, 63.70, 74.95, 125.57, 127.05, 127.22, 128.22, 128.24, 128.28, 139.67, 142.79.

1,6-Di(benzyloxy)hexane (2n)
IR (neat): 2934, 2856, 1454, 1362, 1100, 734, 697 cm^{-1}.

^{1}H NMR: δ = 1.36–1.42 (m, 4 H), 1.56–1.66 (m, 4 H), 3.46 (t, *J* = 6.6 Hz, 4 H), 4.49 (s, 4 H), 7.24–7.35 (m, 10 H).

^{13}C NMR: δ = 26.11, 29.76, 70.38, 72.84, 127.38, 127.53, 128.25, 138.57.

6-Benzyloxyhexyl Benzoate (2o)
IR (neat): 2936, 2858, 1718, 1275, 1111, 712 cm^{-1}.

^{1}H NMR: δ = 1.42–1.50 (m, 4 H), 1.61–1.69 (m, 2 H), 1.74–1.81 (m, 2 H), 3.48 (t, *J* = 6.6 Hz, 2 H), 4.31 (t, *J* = 6.6 Hz, 2 H), 4.50 (s, 2 H), 7.24–7.34 (m, 5 H), 7.40–7.45 (m, 2 H), 7.52–7.57 (m, 1 H), 8.02–8.05 (m, 2 H).

^{13}C NMR: δ = 25.94, 28.71, 29.69, 64.97, 70.22, 72.85, 127.38, 127.50, 128.20, 128.23, 129.41, 130.36, 132.68, 138.48, 166.49.

1, 4-Dibenzyloxybut-2-yl Benzoate (2p)
IR (neat): 2861, 1717, 1452, 1274, 1099, 713 cm^{-1}.

^{1}H NMR: δ = 2.07–2.12 (m, 2 H), 3.54–3.60 (m, 2 H), 3.69 (d, *J* = 4.8 Hz, 2 H), 4.46 (s, 2 H), 4.51 (d, *J* = 12.1 Hz, 1 H), 4.60 (d, *J* = 12.1 Hz, 1 H), 5.45–5.51 (m, 1 H), 7.21–7.30 (m, 10 H), 7.40–7.45 (m, 2 H), 7.53–7.57 (m, 1 H), 8.01–8.04 (m, 2 H).

^{13}C NMR: δ = 31.39, 66.42, 71.16, 71.23, 73.06, 73.11, 127.43, 127.50, 127.59, 128.21, 128.24, 128.25, 129.60, 130.33, 132.78, 138.02, 138.13, 165.97.

1-(Propyloxy)-3-phenylpropane (2q)
IR (neat): 2935, 2857, 1496, 1455, 1118, 745 cm^{-1}.

^{1}H NMR: δ = 0.94 (t, *J* = 7.3 Hz, 3 H), 1.56–1.65 (m, 2 H), 1.86–1.94 (m, 2 H), 2.69 (t, *J* = 7.7 Hz, 2 H), 3.37 (t, *J* = 6.6 Hz, 2 H), 3.42 (t, *J* = 6.6 Hz, 2 H), 7.15–7.30 (m, 5 H).

^{13}C NMR: δ = 10.71, 23.01, 31.38, 32.40, 69.84, 72.57, 125.62, 128.20, 128.39, 141.97.

1-(Pentyloxy)-3-phenylpropane (2r)
IR (neat): 2932, 2858, 1456, 1114, 698 cm^{-1}.

^{1}H NMR: δ = 0.88–0.93 (m, 3 H), 1.30–1.37 (m, 4 H), 1.54–1.62 (m, 2 H), 1.85–1.93 (m, 2 H), 2.69 (t, *J* = 7.7 Hz, 2 H), 3.40 (t, *J* = 6.6 Hz, 2 H), 3.41 (t, *J* = 6.6 Hz, 2 H), 7.16–7.30 (m, 5 H).

^{13}C NMR: δ = 14.12, 22.61, 28.44, 29.52, 31.37, 32.40, 69.87, 70.97, 125.61, 128.18, 128.38, 141.97.

3-(3-Phenylpropyloxy)-1-phenylbutane (2s)
IR (neat): 2928, 2860, 1496, 1454, 1136, 1100, 745 cm^{-1}.

^{1}H NMR: δ = 1.16 (d, *J* = 6.2 Hz, 3 H), 1.66–1.76 (m, 1 H), 1.81–1.94 (m, 3 H), 2.61–2.79 (m, 4 H), 3.30–3.55 (m, 3 H), 7.15–7.30 (m, 10 H).

^{13}C NMR: δ = 19.75, 31.78, 31.91, 32.53, 38.50, 67.47, 74.52, 125.57, 125.63, 128.20, 128.21, 128.32, 128.38, 142.00, 142.32.

1-Cyclohexyloxy-3-phenylpropane (2t)
IR (neat): 2931, 2855, 1451, 1363, 1108 cm^{-1}.

^{1}H NMR: δ = 1.15–1.32 (m, 5 H), 1.50–1.57 (m, 1 H), 1.70–1.77 (m, 2 H), 1.84–1.94 (m, 4 H), 2.69 (t, *J* = 7.7 Hz, 2 H), 3.15–3.23 (m, 1 H), 3.45 (t, *J* = 6.6 Hz, 2 H), 7.15–7.29 (m, 5 H).

^{13}C NMR: δ = 24.30, 25.91, 31.75, 32.42, 32.45, 66.91, 77.49, 125.57, 128.16, 128.39, 142.06.

References

(1) Greene, T. W.; Wuts, P. G. M. In *Protective Groups in Organic Synthesis*, 3rd ed.; Wiley: New York, **1999**, Chap. 2.

(2) (a) Czernecki, S.; Georgoulis, C.; Provelenghiou, C.; Fusey, G. *Tetrahedron Lett.* **1976**, 3535. (b) Takaku, H.; Kamaike, K. *Chem. Lett.* **1982**, 189. (c) Kanai, K.; Sakamoto, I.; Ogawa, S.; Suami, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1529. (d) Fukuzawa, A.; Sato, H.; Masamune, T. *Tetrahedron Lett.* **1987**, *28*, 4303. (e) Grice, P.; Ley, S. V.; Pietruszka, J.; Priepke, H. W. M.; Warriner, S. L. *J. Chem. Soc., Perkin Trans. 1* **1997**, 351.

(3) Freedman, H. H.; Dubois, R. A. *Tetrahedron Lett.* **1975**, 3251.

(4) (a) Oriyama, T.; Kimura, M.; Oda, M.; Koga, G. *Synlett* **1993**, 437. (b) Oriyama, T.; Oda, M.; Gono, J.; Koga, G. *Tetrahedron Lett.* **1994**, *35*, 2027. (c) Oriyama, T.; Kimura, M.; Koga, G. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 885. (d) Oriyama, T.; Yatabe, K.; Kawada, Y.; Koga, G. *Synlett* **1995**, 45. (e) Oriyama, T.; Yatabe, K.; Sugawara, S.; Machiguchi, Y.; Koga, G. *Synlett* **1996**, 523. (f) Oriyama, T.; Noda, K.; Yatabe, K. *Synlett* **1997**, 701. (g) Oriyama, T.; Noda, K.; Sugawara, S. *Synth. Commun.* **1999**, *29*, 2217. (h) Suzuki, T.; Ohashi, K.; Oriyama, T. *Synthesis* **1999**, 1561. (i) Suzuki, T.; Oriyama, T. *Synthesis* **2001**, 555. (j) Suzuki, T.; Kobayashi, K.; Noda, K.; Oriyama, T. *Synth. Commun.* **2001**, *31*, 2761. (k) Oriyama, T.; Kobayashi, K.; Suzuki, T.; Oda, M. *Green Chem.* **2002**, *4*, 30. (l) Kobayashi, K.; Watahiki, T.; Oriyama, T. *Synthesis* **2003**, 484.

(5) (a) Kato, J.-I.; Iwasawa, N.; Mukaiyama, T. *Chem. Lett.* **1985**, 743. (b) Sassaman, M. B.; Kotian, K. D.; Surya Prakash, G. K.; Olah, G. A. *J. Org. Chem.* **1987**, *52*, 4314. (c) Hatakeyama, S.; Mori, H.; Kitano, K.; Yamada, H.; Nishizawa, M. *Tetrahedron Lett.* **1994**, *35*, 4367. (d) Bajwa, J. S.; Jiang, X.; Slade, J.; Prasad, K.; Repič, O.; Blacklock, T. J. *Tetrahedron Lett.* **2002**, *43*, 6709. (e) Chandrasekhar, S.; Chandrashekar, G.; Nagendra Babu, B.; Vijeender, K.; Venkatram Reddy, K. *Tetrahedron Lett.* **2004**, *45*, 5497.

(6) (a) Watahiki, T.; Oriyama, T. *Tetrahedron Lett.* **2002**, *43*, 8959. (b) Watahiki, T.; Akabane, Y.; Mori, S.; Oriyama, T. *Org. Lett.* **2003**, *5*, 3045. (c) Iwanami, K.; Oriyama, T. *Chem. Lett.* **2004**, *33*, 1324. (d) Iwanami, K.; Seo, H.; Tobita, Y.; Oriyama, T. *Synthesis* **2005**, 183.

(7) Sajiki, H.; Hirota, K. *Tetrahedron* **1998**, *54*, 13981.

(8) Akiyama, T.; Hirofuji, H.; Ozaki, S. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1932.

(9) Ochiai, M.; Ito, T.; Takahashi, H.; Nakanishi, A.; Toyonari, M.; Sueda, T.; Goto, S.; Shiro, M. *J. Am. Chem. Soc.* **1996**, *118*, 7716.